Oxidation Resistance of Boiler Steels with Al_2O_3 – Y_2O_3 Nano- and Micro-Composite Coatings Produced by Sol–Gel Process

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Al_2O_3 – Y_2O_3 nano- and micro-composite coatings have been deposited on boiler steel substrates using sol–gel composite coating technology. The processes include dipping samples in a sol–gel solution dispersed with fine ceramic powders, which is prepared by high-energy ball milling. Scanning electron microscopy (SEM) and XRD analyses show that the one-layer coating (*i.e.* dipping for one time) has a thickness of more than 2 μm . The coating is mainly composed of α - Al_2O_3 and γ - Al_2O_3 , and is relatively dense without cracking after drying and sintering treatments. The oxidation tests performed in air at 600°C show that the coatings possess much improved resistance to high temperature oxidation and scale spallation. It is believed that the nano-structured composite particles and reactive elements are integrated into the coatings, which played an important role in improving their oxidation resistance.

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1. Introduction

The sol–gel process has several advantages over other fabrication methods such as plasma spraying and physical vapor deposition (PVD). It is simple, economically feasible and allows coatings of complex geometry. Sol–gel oxide coatings or films have found wide applications as functional materials in optics, microelectronics, and photo-electronics, and for the purpose of protection.^{1–5)} However, sol–gel technology has never reached its full industrial potential due to some limitations: the thickness of films produced by this method is often thinner than 0.5 μm due to the shrinkage and cracking problems during drying and sintering; and thick films are easy to spall off because of the poor adhesion to the substrates.

The sol–gel composite coating technique, which is also called an improved sol–gel process for producing thick and large area ceramic coatings on a wide range of substrates, is a relatively new method.^{6–8)} One or two selected fine ceramic powders are dispersed into a sol–gel solution to form a uniform and stable paint. Ceramic powders may be selected from various materials, including alumina, zirconia, silica, titania, silicon carbide and titanium carbide. The paints prepared may be applied to any suitable substrate either by dipping, spinning or spraying as the conventional sol–gel methods. Upon firing, the sol–gel derived phase acts to bind the powder phase internally and to the substrate. This technique combines chemical (sol–gel) and physical (high energy ball milling) methods, producing uniform composite layers of controlled thickness on metallic or ceramic substrates. Sol–gel composite coatings have different applications including protecting metals from heat, corrosion and erosion, and providing electrical insulation, etc.

Among oxide ceramic coatings Al_2O_3 coatings have been extensively studied because of its good properties such as excellent chemical stability, high mechanical strength and

hardness,^{9,10)} superior corrosion resistance, and good insulating property.^{11–13)} Although Al_2O_3 coatings have excellent oxidation resistance, they may suffer from scale spallation in service due to the thermal stress between the coatings and substrates. A small addition of Y_2O_3 to Al_2O_3 can change the mass transfer mechanism in the process of oxidation, reducing the formation of holes at the interface, and improving the adhesion of the scale to the substrate.^{14,15)}

In this work, we adopted an improved sol–gel composite process to prepare relatively thick Al_2O_3 – Y_2O_3 nano- and micro-composite coatings. The oxidation and spallation resistance of these coatings on boiler steels were investigated.

2. Experimental

The sol–gel is prepared by co-precipitation. The solution contained 2 g of $\text{Al}(\text{NO}_3)_3 + 1 \text{ mass\% Y}(\text{NO}_3)_3$ dissolved in 50 ml of deionized water. Ammonia water was then added under stirring to adjust the pH value of the solution. The viscosity of the solution was adjusted by addition of polyvinyl alcohol. α - Al_2O_3 powders were prepared by high-energy ball milling for 4 h at 600 r/min, which produced powders with the size of 25 nm and 50 μm . The α - Al_2O_3 powders were loaded to the solution by 50 mass%. The mixture of sol–gel and α - Al_2O_3 powders was applied to boiler steel by dipping as in conventional sol–gel method. The coating on the substrate for each dipping is heated in air at 400°C for 30 min. In order to achieve thick films, this process was repeated for a few times.

Fe–5Cr–Mo (mass%) boiler steel specimens were cut to a size of 20 × 15 × 3 mm. All surfaces of the specimens were polished with 800 grit SiC paper, followed by ultrasonic cleaning with alcohol and deionized water.

High temperature oxidation of the specimens was carried out in a horizontal furnace at 600°C in air for 100 h. The specimens were placed in quartz crucibles, which had been

Fig. 1 SEM micrographs of $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ sol-gel composite coatings on substrates after an annealing at 600°C in air for 3 h: (a) cross section; (b) surface.

heated until the mass didn't change any more. After a certain time period, mass gains were weighed using an electronic balance with an accuracy of 10^{-5} g. Oxidation kinetic curves were plotted separately by using the mass gains and scale spallation mass of the specimens vs. time. XRD spectra were recorded using $\text{Cu-K}\alpha$ radiation to analyze the phase and composition of the oxides. The surface and the cross-section morphology of the oxides were observed using SEM.

3. Results

Figure 1(a) shows the SEM cross section micrograph of $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ sol-gel composite coatings on substrates heated at 600°C in air for 3 h. It shows that the one-layer coating (after one dipping) is $\sim 2.3\ \mu\text{m}$ thick, and the coating is dense. Figure 1(b) shows the SEM surface micrograph of $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ sol-gel composite coatings heated at 600°C in air for 3 h. The coating is composed of composite particle clusters with an average diameter of $\sim 1\ \mu\text{m}$. The clusters consist of larger particles having an average diameter of $\sim 0.5\ \mu\text{m}$ in center and smaller particles of $\sim 80\ \text{nm}$ surrounding the larger ones.

Figure 2 shows the XRD spectra of $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ composite coatings after heating at 600°C for 3 h. The oxide coatings were mainly composed of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$.

Oxidation kinetics of Fe-5Cr-Mo boiler steel substrates with and without coatings at 600°C in air for 100 h is illustrated in Fig. 3. It can be seen that the $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ composite coatings significantly improved the oxidation resistance of the steel. The steel sample without coating shows a linear kinetics with a mass gain of $\sim 8 \times 10^{-3}\ \text{Kg/m}^2$ after exposure at 600°C for 100 h, compared to $\sim 6 \times 10^{-4}\ \text{Kg/m}^2$ for the specimen coated with one-layer $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ and almost no mass gain for the specimen coated with a 3-layer $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ coating [Fig. 3(a)]. The coatings also improve the scale spallation resistance of the steel although the total amount of spallation is not high. The uncoated sample has a scale spallation of $1.2 \times 10^{-3}\ \text{kg/m}^2$, while the coated samples have spallations ranging from only 3 to $5 \times 10^{-4}\ \text{kg/m}^2$ as shown in Fig. 3(b). Therefore, the composite coatings show significant improvement to the oxidation resistance. The results also indicate that the thickness of the coatings is important for protection.

Fig. 2 XRD spectra of $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ sol-gel composite coatings after an annealing at 600°C in air for 3 h.

The SEM surface morphology of the oxide scales after oxidation is shown in Fig. 4. The alloy without coatings shows a rough surface with two types of areas: the bright and dark areas as shown in Fig. 4(a). The bright areas are oxide whiskers containing mainly Cr and Fe oxides; the dark areas are holes and pores, implying that the scales have been broken away. The specimen with coatings shows a flat scale of Al oxides with a few small ridges as shown in Fig. 4(b). No scale spallation could be seen.

4. Discussions

4.1 Effects of nano- and micro-composite particles

The nano- and micro-composite coatings play an important role in resisting oxidation of substrates. It is known that nano-sized particles have special properties such as toughening and strengthening ceramic materials, enhancing the adherence between coatings and substrates, preventing crack initiation, and resisting oxidation and hot corrosion.^{16,17)} However, they are easy to form aggregation because of the high surface energy, losing the special properties of the nanometer materials.

In our work, $\alpha\text{-Al}_2\text{O}_3$ micron particles dispersed in an Al_2O_3 and Y_2O_3 sol-gel solution. High-energy ball milling drives the particles of two sizes to form uniform composite

Fig. 3 Oxidation kinetic curves of the coated and uncoated boiler steel samples. The oxidation was conducted in air at 600°C for 100h: (a) Mass gain vs. time; (b) Spallation mass loss vs. time.

Fig. 4 SEM micrograph of the coated and uncoated boiler steel samples after oxidation in air at 600°C for 100h: (a) uncoated steel sample; (b) coated with $\text{Al}_2\text{O}_3\text{--Y}_2\text{O}_3$.

Fig. 5 Schematic drawing of the composite particles formed by sol-gel, high energy ball milling and sintering.

clusters, which can effectively avoid the aggregation of the nanometer particles and keep their special characteristics. Figure 5 shows a schematic drawing of the formation of the nano-structured composite particle clusters. Micro-sized particles are surrounded by nano-sized particles to form strong clusters in the coatings, as shown in Fig. 1(b).

It can also be seen that the adherence between the coatings and alloy substrates is good. Due to the existence of the composite particles in the sol-gel, less shrinkage occurs when the coating is formed. The composite particles can also act as crack inhibitors. The hydroxyl groups in the solution on both substrate and ceramic powder can strongly bond them together, resulting in a dense structure. Furthermore,

although the nano- Al_2O_3 particles derived from sol-gel is composed of $\gamma\text{-Al}_2\text{O}_3$ which may cause phase transformation at high temperature, the micro- Al_2O_3 particles added to sol-gel is composed of $\alpha\text{-Al}_2\text{O}_3$. Therefore, the phase structure of composite clusters may not change much during sintering stage. All above factors lead to crack-free protective coatings, consequently resulting in effective protection against oxidation.

4.2 Synergic effects of Al_2O_3 and Y_2O_3

The results indicate that $\text{Al}_2\text{O}_3\text{--Y}_2\text{O}_3$ composite coatings have excellent high temperature oxidation resistance. Al_2O_3 films act as a good diffusion barrier for oxygen, but Al_2O_3

layers may spall away after a long time exposure to high temperatures and/or during cooling due to the high thermal stress between the coatings and alloy substrates. The main effects of the addition of yttrium were to favor oriented rather than random scales and grain boundary rather than intergranular pores in the oxide scale.¹⁸⁾ In addition, the addition of Y_2O_3 can change the diffusion mechanism of Al_2O_3 coatings during oxidation process, enhancing the inward diffusion of oxygen ions and suppressing the outward diffusion of metal ions.¹⁹⁾ This change reduces the holes produced at the scale/alloy interface, enhancing the adherence of the coatings to the alloy substrates, and therefore significantly improving the high temperature oxidation resistance of the coating-substrate system.

5. Conclusions

- (1) Al_2O_3 - Y_2O_3 ceramic coatings with excellent adhesion to the substrate can be obtained using an improved sol-gel composite ceramic coating process. The coatings are mainly composed of α - Al_2O_3 and γ - Al_2O_3 with a dense structure. One-time dipping produces a single-layer coating of more than 2 μm thick; and multi-dipping can produce much thicker coatings.
- (2) These composite coatings show significantly improved high temperature oxidation resistance when they are applied to a boiler steel. The nano- and micro-structured oxide clusters play an important role in reducing the oxidation rate and scale spallation tendency.
- (3) Sol-gel composite coating method has the advantages of simple equipment, inexpensive process, allowing coating of complex geometry, and producing thick ceramic coatings with less cracking tendency. It is a promising technique that can be used to produce

protective coatings, thermal barrier coatings, and coatings for electrical insulation.

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